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THERMAL CRACKING OF PHENOLIC-NYLON PYROLYSIS PRODUCTS ON PASSING THROUGH A HEATED CHAR

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16. Abstract

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THERMAL CRACKING OF PHENOLIC-NYLON PYROLYSIS
PRODUCTS ON PASSING THROUGH A HEATED CHAR

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SUMMARY

An analysis of the thermal cracking of phenolic-nylon pyrolysis products on passing through a simulated char has been performed. The pyrolysis products were generated by flash pyrolysis of the heat-shield material in front of the heated char and were analyzed, after passing through the char, by gas chromatography. The change in composition of the pyrolysis products after passing through the char showed that the high molecular weight products cracked to lower molecular weight products, beginning at about 700° C. The low molecular weight products were found to increase with increasing char temperature and, at char temperatures approaching 1000° C, the pyrolysis gases were composed of carbon dioxide, carbon monoxide, water, methane, hydrogen, acetylene, benzene, and cyclopentanone.

INTRODUCTION

An important part of the thermal protection provided by charring ablation materials is the transpiration cooling which occurs as the products of heat-shield degradation percolate through the heated char. The heat protection provided by this phase of the ablation process results from absorption of energy as the pyrolysis products increase in temperature and undergo thermal cracking to lower molecular weight products. The efficiency of this mechanism can to a large degree be determined by the type and quantity of products which are generated by polymer decomposition. Lower molecular weight products from degradation are desired since these products absorb more energy on passage through the hot char and also provide efficient blocking as they enter the boundary layer surrounding the heat shield. However, in actual cases the degradation products generated at the pyrolysis zone are high molecular weight species such as phenols, benzene, and long chain depolymerization-type products. (See ref. 1.)

There have been several investigations to determine the type and degree of interaction between pyrolysis gases and the heated char. In these experiments, however, the pyrolysis gases were simulated by a single organic product such as methane. (See refs. 2 and 3.) The results from these experiments were then used to estimate the degree

of cracking of the actual pyrolysis products and thus the final gas composition injected into the boundary layer. Other attempts to predict the mechanism in heated char that results in changes in the composition of gases passing through it include equilibrium calculations, such as those of references 4 and 5, where the results have been used in conjunction with a transient numerical analysis of ablation materials.

In the present investigation, the low-temperature initial cracking of actual pyrolysis products has been studied. The temperature range employed (from about 600° C to 1000° C) represents only the lower limits of char temperatures, which may exceed 3000° C at points near the ablating surface. The present investigation differs from previous studies because actual pyrolysis gases were used. In the present study, a small sample of a charring ablation material, low-density phenolic nylon, was vaporized in front of a heated char. The pyrolysis products were carried through the heated char by a stream of helium (carrier gas) and continued uninterrupted to a vapor-phase chromatograph. The char temperature was varied between about 600° C and 1000° C and, as the temperature increased, the change in compositon of the pyrolysis products showed that most of the products were affected by the hot char. The composition of the gases after passing through the char was compared with an analysis of the products produced from heat-shield pyrolysis.

In addition to studies of the gas composition change with char temperature, some measurements were made of the differential pressure across the char as the pyrolysis products passed through the char.

The units for the physical quantities used in this paper are given in the International System of Units (SI). Reference 6 presents factors relating the International System with other frequently used system of units.

MATERIALS

The heat-shield material studied in this investigation was a low-density composite of phenolic and nylon. The composite actually contained two phenolic components: a novolac-derived material added to the premolded mixture to serve as binder and a resole-derived polymer in the form of small (approximately 100-micrometer diameter) hollow spheres. In final molded form the composite had a density of about 560 kg/m^3 and was composed by mass of 40-percent nylon, 35-percent phenolic microspheres, and 25-percent phenolic binder. All components were purchased from commercial sources. The fabrication procedure for this material and a more complete description of each component are given in reference 7.

The thermophysical properties of the molded composite are given in reference 8 and the chemical properties associated with each individual component are given in

reference 7. An evaluation of the thermal degradation for this material is given in references 3, 9, and 10.

The char was simulated by a commercially supplied porous carbon. Table I gives a summary of the properties of this material and also the comparable properties for an actual phenolic-nylon char. (See ref. 11.) The carbon char thickness for these experiments was 0.50 cm.

TABLE I.- PHYSICAL PROPERTY DATA FOR CARBON

AND PHENOLIC-NYLON CHARS

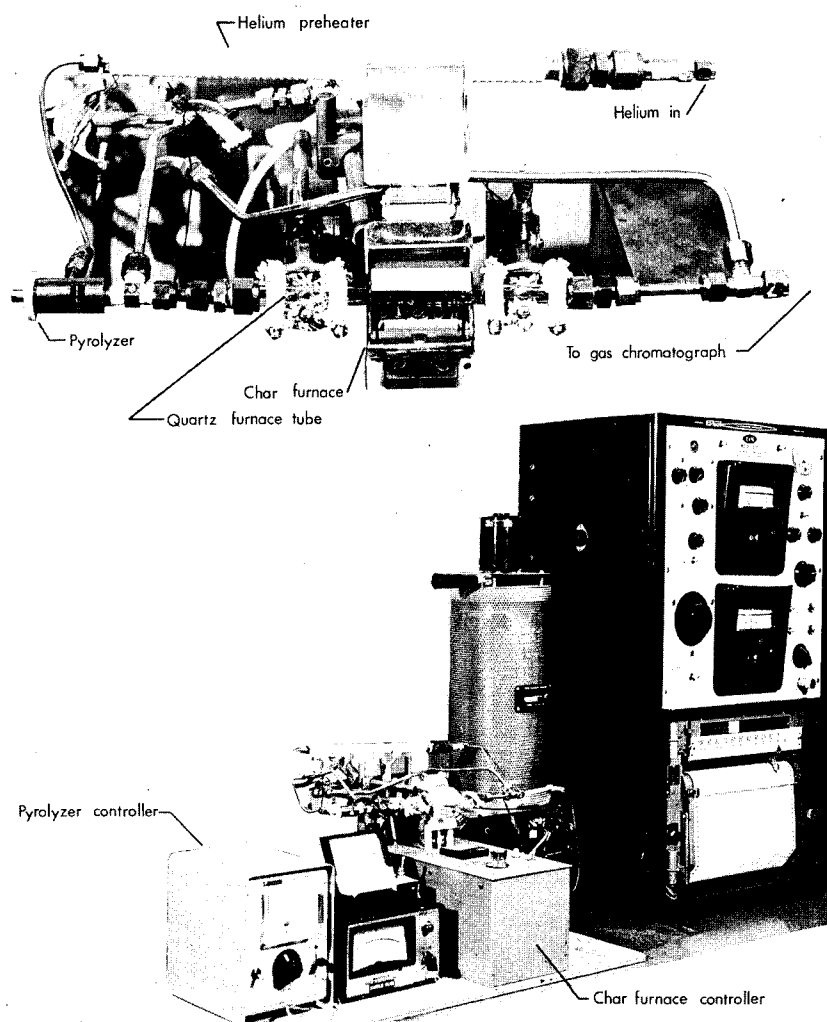| Material	Porosity	Mean pore diameter, μm	Admittance,[1] cm^2/sec
Carbon char	0.47	20	374
Phenolic-nylon char[2]	0.80	40	12 219

[1]Measured at room temperature in helium (ref. 11).
[2]Arc-jet and furnace produced.

APPARATUS AND TEST PROCEDURE

The apparatus employed in this investigation is shown in figure 1. In the lower part of figure 1 are shown the gas chromatograph and the cracking study apparatus. The upper part of this figure provides an enlarged photograph of the cracking study apparatus. This section of the apparatus is also shown schematically in figure 2. It consists of a helium preheater, ablation material pyrolyzer, isothermal reactor, a differential pressure transducer, and a gas chromatograph. All tubing connections between each component of the apparatus were of stainless steel and each section of tubing was wrapped with heating tapes which maintained each connecting section at 250° C. Maintaining each section at 250° C reduced carrier gas cooldown and condensation of the degradation products.

The helium preheater was constructed of a 35-cm section of 3-cm o.d. stainless-steel tubing filled with small aluminum oxide (Al_2O_3) chips. The preheater was maintained at 275° C throughout each test.

The ablation material pyrolyzer consisted of a platinum-coil heater approximately 0.5 cm in length and 0.2 cm in diameter. The ablation material sample, usually about 2 mg in mass, was wedged tightly into the center of the heater coil and was pyrolyzed by

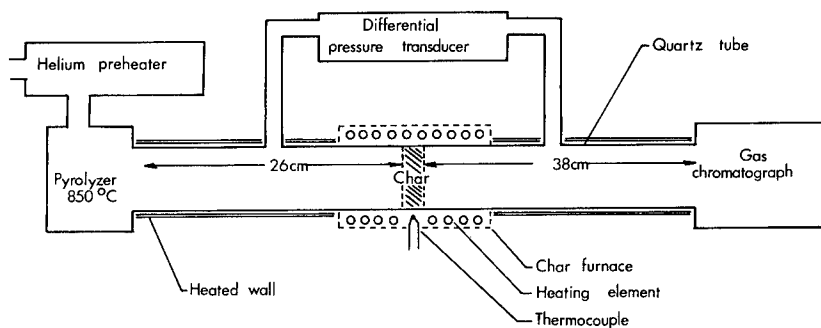Figure 1.- Photograph of gas chromatograph and cracking
study apparatus.

Figure 2.- Schematic drawing of apparatus used for the
pyrolysis product cracking study.

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applying current to the heater coil. The current through the coil was maintained for
10 seconds in each test and was sufficient to bring the specimen temperature from 250° C
(carrier gas temperature) to 850° C. The coil temperature had been previously cali-
brated, as described in reference 9, by using the known melting points of several organic
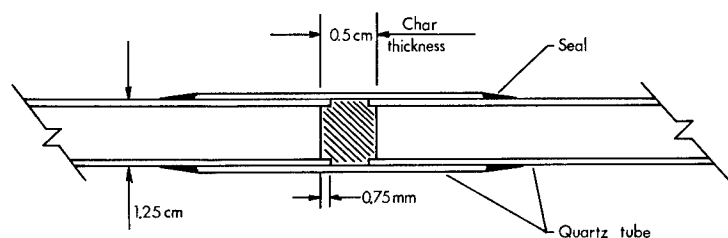and inorganic materials.

Figure 3.- Drawing of char mounting in quartz furnace tube.

Figure 3 shows a drawing
of the quartz furnace tube and
the method employed to seal the
char specimen inside the tube.
The char specimen was machined
to 0.5-cm thickness and to the
shape shown in figure 3. The
machined char specimen was
then placed at the ends of two
concentric tubes as shown and, once in place, the outer tube was fused at the ends to the
inner quartz tubes. During the sealing process both of the inner tubes were forced
tightly against the char specimen and helium was purged through the tube to prevent char
oxidation.

A resistance furnace approximately 7.5 cm long with a 2-cm opening through the
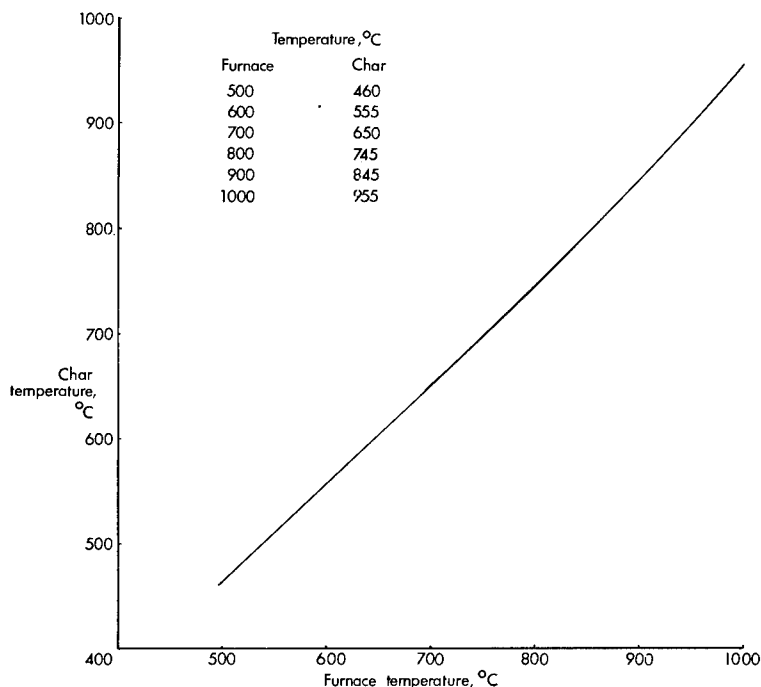center was used to heat the char specimen. The temperature of the furnace was deter-
mined by a thermocouple in
the center of the furnace
immediately below the char
specimen on the outside of the
quartz furnace tube. The
thermocouple position is
shown in figure 2. The actual
char temperature was deter-
mined by bonding a thermo-
couple to the back and front
face of the char with a high-
temperature cement. The
char-temperature calibration
obtained is shown in figure 4.
As shown, the char tempera-
ture was found to be approxi-
mately 50° C below any given
furnace temperature between

Temperature,$^{\circ}$C	
Furnace	Char
500	460
600	555
700	650
800	745
900	845
1000	955

Figure 4.- Furnace temperature calibration.

600° and 1000° C. No difference could be determined between the front and back surface temperatures of the char.

A capacitance-type differential pressure transducer was connected across the char specimen as shown in figure 2. This transducer was sensitive to changes as small as 4.0 mN/m^2. During operation the differential pressure (Δp) across the char was established before sample vaporization. Once a stable baseline was established (flow rates and char temperature stable), the sample was vaporized and the differential pressure across the char was then continuously measured until 4 minutes after the products passed through the char.

The gas chromatograph employed during the investigation is described in reference 9. Basically, it is a programed temperature (maximum column temperature 500° C) thermal conductivity apparatus which uses 0.65-cm o.d. columns. The injection port, which was connected directly to the isothermal reactor, was maintained at 300° C. Many columns were used for the selected separation of the degradation products and these products are listed in table II along with the products separated. The quantity of each product present was determined by calibration of the gas-chromatograph thermal conductivity detector. The calibration was accomplished by successive injections of the pure identified product to determine the detector response to each product.

TABLE II.- SUMMARY OF GAS CHROMATOGRAPH COLUMNS

AND PRODUCTS SEPARATED

Column used	Products separated	Chromatograph conditions
Activated charcoal	H_2, N_2, CH_4, CO, CO_2	Programed from 50° C to 290° C at 0.35° C/sec; Sensor: 150 mA; Flow rate: 1.12 cm^3/sec
Apiezon L on teflon	Phenol methylphenols	Isothermal at 75° C for 2.5 min; Programed at 0.18° C/sec to 200° C; Sensor: 150 mA; Flow rate: 1.0 cm^3/sec
Carbowax 20 M on teflon	Water	Isothermal at 85° C; Sensor: 150 mA; Flow rate: 1.0 cm^3/sec
Dowfax 9N9/KOH on chromosorb P	Ammonia	Isothermal at 100° C; Sensor: 150 mA; Flow rate: 1.0 cm^3/sec

Tests were performed at 100° C increments for furnace temperatures from 600° C to 1000° C. At each temperature three or four tests were performed and the results shown are the average of these tests.

The gas flow rate was measured by a mass flow meter which was calibrated for helium. The flow was measured approximately 1 meter from the exit port of the gas chromatograph and at ambient temperature (25° C).

After completion of all testing, the char specimen was removed from the quartz tube and vacuum-molded in epoxy. Photomicrograph techniques were employed to determine whether carbon deposition had occurred in the pores of the char specimen.

RESULTS AND DISCUSSION

Determination of Operating Conditions

It has been determined from mass loss studies, such as those of reference 10, that typical mass flow rates through the ablative char are much higher than those obtainable in the present experiment. In the present experiment, flow rate was limited by the gas chromatograph and the design of the cracking study apparatus. For simulation of actual
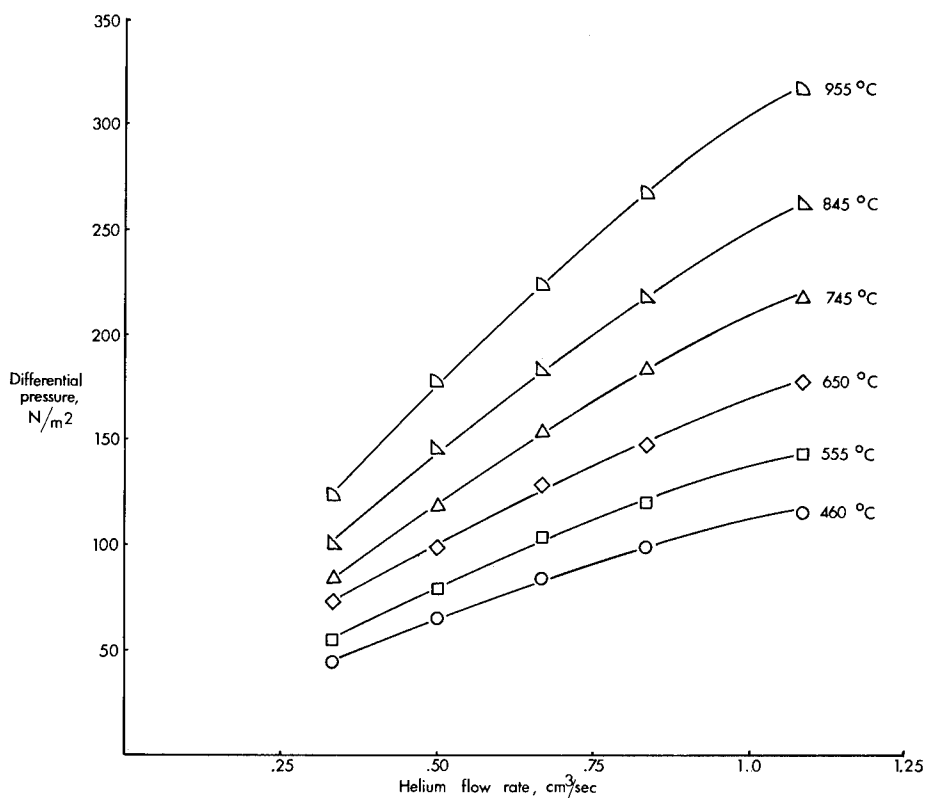

Figure 5.- Effect of flow rate and temperature upon the differential pressure across the 0.5-cm char.

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flow through a char, flow rates of the order of 100 cm^3/sec would be required. The maximum flow rate obtainable, however, in these experiments was 1.1 cm^3/sec and therefore the chemical reactions which occurred (cracking reactions) should more nearly approach chemical equilibrium conditions.

The flow rates obtainable in the experimental apparatus are shown in figure 5, where the interaction of flow rate and differential pressure across the char specimen is shown for char temperatures from 460° C to 955° C. The data shown in figure 5 were obtained with a helium inlet temperature of 250° C and an internal pressure of 207 kN/m^2. As the results in figure 5 indicate, for flow rates beyond 0.83 cm^3/sec, all the data deviate appreciably from a straight line. Because of this deviation, a flow rate of 0.83 cm^3/sec was used for all tests in this investigation.

<center>Analysis of Gaseous Products</center>

Degradation of organic materials produces a variety of products which range from high molecular weight depolymerization-type products to simple hydrocarbon gases such as methane. (See ref. 1.) When several organic materials that vary in molecular structure are combined, as in most low-density charring ablation materials, the degradation pattern (pyrolysis product distribution) becomes varied and very complex because of the wide variety and small quantities of individual species. For low-density phenolic nylon of the composition used in this investigation, many of the degradation products have been determined and are shown in table III. The product distribution was obtained by flash pyrolysis of the heat-shield material at 850° C in the entrance port of the gas chromatograph. The products which were observed are given along with their structure, molecular weight, and the mass percent found. A temperature of 850° C was used because mass loss data indicate degradation to be complete at this temperature. (See ref. 10.)

For the products observed, the molecular weights ranged between 2 and 136 and the mean molecular weight (number average) was about 37. As shown in reference 9, the high molecular weight products result principally from phenolic degradation (binder and microspheres). All the products identified amount to approximately 50 percent of the original mass of undegraded material. Reference 10 has shown from mass loss data that the char residue from degradation of low-density phenolic nylon accounts for 34 percent of the original mass. Sixteen percent of the original mass was thus unaccounted for in these studies and was assumed to have been high molecular weight species that condensed and were not passed through the gas chromatograph columns. These unidentified products, however, are most likely present in the products which were injected into the char and therefore could contribute to the final composition observed in the gas chromatograph. The products shown in table III are the major gaseous products and therefore

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TABLE III.- PRODUCTS FROM FLASH PYROLYSIS

OF PHENOLIC-NYLON AT 850° C

Product	Structure	Molecular weight	Mass percent
Phenol	C_6H_5OH	94.11	12.4
Carbon dioxide	CO_2	44.01	8.7
Methylphenol	$C_6H_4CH_3OH$	108.13	6.7
Water	H_2O	18.01	5.9
Dimethylphenol	$C_6H_3(CH_3)_2OH$	122.16	4.9
Trimethylphenol	$C_6H_2(CH_3)_3OH$	136.09	4.0
Carbon monoxide	CO	28.01	2.5
Cyclopentanone	C_5H_8O	84.11	1.9
Methane.	CH_4	16.04	1.0
Hydrogen	H_2	2.01	1.0
Benzene	C_6H_6	78.11	0.4
Ammonia	NH_3	17.02	0.2
Formaldehyde	CH_2O	30.02	Trace
Total products, percent			49.6
Char, percent			34.0
Unaccounted for, percent			16.3

are of principal interest in this investigation since these products comprise about 74 per-
cent of the gases which initially begin to percolate out of the pyrolysis zone and toward
the hot char surface of an ablating material.

The variations in low molecular weight products present in the gas after passing
through the char at various temperatures are shown in figure 6. It should be noted that
data were taken at approximately 100° C intervals from about 550° C to 950° C. Smooth
curves have been drawn through these data points.

All the products, with the exception of carbon dioxide, show increases with
increasing char temperature. Carbon dioxide remains nearly constant at 8.7 percent
with only a very light decrease observed over the temperature range from 750° C to
950° C.

Cyclopentanone exhibits some unusual characteristics which have not been com-
pletely explained. The increase in C_5H_8O begins between 650° C and 750° C and con-
tinues to 850° C after which there is a decrease to 3.5 percent at 950° C. The increase
in cyclopentanone after 650° C is surprising since it is a product with a relatively large
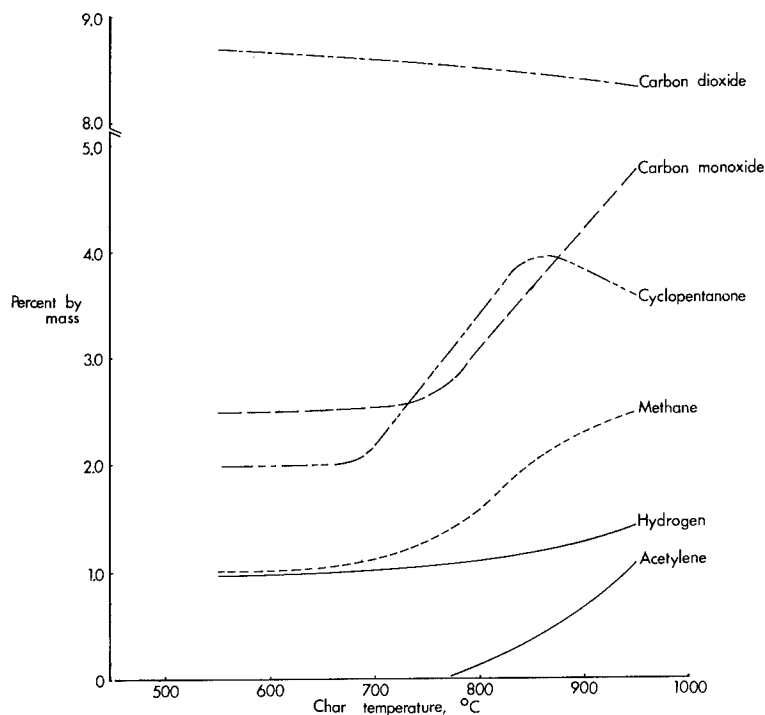
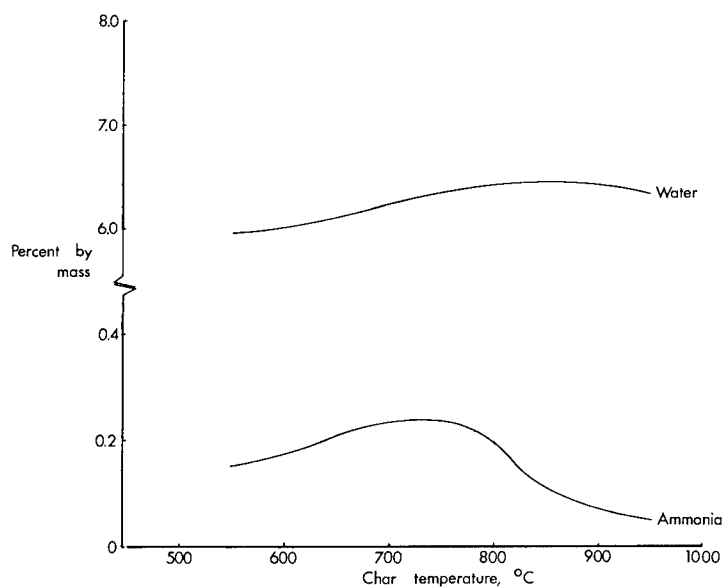Figure 6.- Variation of low molecular weight pyrolysis products with temperature.

Figure 7.- Variation of pyrolysis products with temperature.

molecular weight. One possible explanation for the increase in this product involves the decomposition of a larger unidentified product to cyclopentanone at temperatures below 850° C whereas, at a higher temperature, breakdown follows an alternate path to lower molecular weight species.

Methane, hydrogen, and acetylene each show increases in the quantity observed. Acetylene, which was not detected in the pyrolysis gases, appears after 750° C and is present at greater than 1 percent at 950° C. Traces of ethylene were also detected after 800° C; however, they are not shown. The effects of char temperature on other low molecular weight species, water and ammonia (found in the effluent gas), are shown in figure 7. Water in the pyrolysis gases was found to increase slowly from an initial 5.9 percent to a maximum of about 7 percent at 850° C; thereafter a decrease was observed. Ammonia was found to increase from 0.15 percent at 550° C to a maximum of 0.25 percent at 750° C and thereafter decreased.

The mass fractions of the high molecular weight products present after passing through the char at various temperatures

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are shown in figure 8. As stated previously, the high molecular weight products result principally from phenolic degradation and are shown as methyl-substituted phenols. The products vary in molecular weight between 94 and 136. Figure 8 shows the decrease observed in phenol, methylphenol, dimethyphenol, and trimethylphenol. The curves of figure 8 show that the decrease observed begins at a lower temperature as the molecular weight increases. For phenol the decrease begins principally after 750° C whereas methylphenol and dimethylphenol quantitatively decrease after 700° C and 650° C, respectively. Through this temperature range, trimethylphenol exhibited a slight increase to 650° C and thereafter decreased to 850° C.
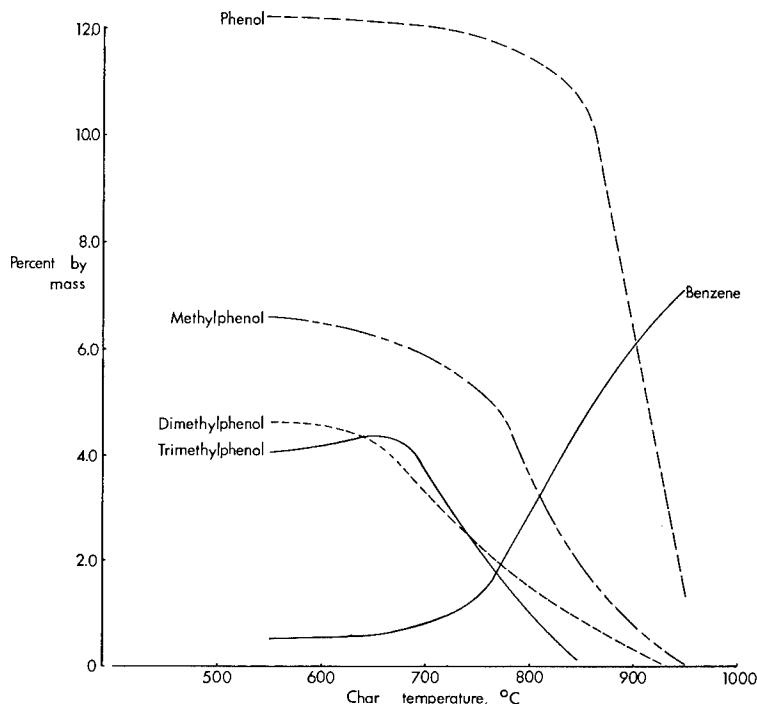
Figure 8.- Effect of char temperature upon the high molecular weight products.

Also shown in figure 8 is the change in quantity of benzene present as the char temperature was increased. Originally, benzene was present as only 0.4 percent of the pyrolysis gases; however, as figure 8 indicates, this quantity increased to approximately 7 percent at 950° C. These data indicate that the methyl-substituted phenols undergo thermal cracking on passing through the char to produce principally benzene. Corresponding to the increase in benzene and the decrease in methyl-substituted phenols was the increase in low molecular weight species such as methane and hydrogen which was shown in figure 6.

The results of gas composition analysis indicate that the gas species which are injected into the latter (outer) parts of an actual heat-shield char are considerably different from the composition of the original pyrolysis products as given in table III.

The species which exist after passing through a char section at 950° C are shown in table IV. These products are, in order of decreasing quantities: carbon dioxide, benzene, carbon monoxide, cyclopentanone, methane, hydrogen, water, and acetylene. With the exception of benzene and cyclopentanone, these products are all low molecular weight products. As table IV shows, the mass of products found after passing through

TABLE IV.- COMPOSITION OF GASES AFTER PASSING THROUGH CHAR AT 950° C

Product	Structure	Mass, percent
Carbon dioxide	CO_2	8.4
Benzene	C_6H_6	7.1
Carbon monoxide	CO	4.7
Cyclopentanone	C_5H_8O	3.6
Methane	CH_4	2.5
Hydrogen	H_2	1.4
Water	H_2O	1.2
Acetylene	C_2H_2	1.1
Ethylene	C_2H_4	0.55
Methylphenol	$C_6H_4CH_3OH$	0.1
Ammonia	NH_3	0.01
Total products, percent		30.7
Mass of products lost during passage through char, percent		18.9
Total products from pyrolysis, percent		49.6

the char was about 31 percent. Thus, approximately 19 percent was lost during passage through the char. Part of this lost quantity was found as carbon deposition and is discussed in a following section.

The change in composition of the pyrolysis gases observed with increases in char temperature is reflected in the mean molecular weight of the products as shown in figure 9. This figure shows the number average molecular weight of the products after passing through the char along with the results predicted by chemical equilibrium calculations. The equilibrium calculations were obtained from reference 5. The data from this reference include all possible products and no loss of material is allowed. Since some loss of products occurred in the present investigation, the product analysis at each temperature was used to recalculate the chemical equilibrium composition as in reference 5. The results of these calculations are also shown in figure 9. As shown, the mean molecular weight, determined experimentally, decreases from 37 to 21 as the char temperature increases to 950° C and tends to be approaching chemical equilibrium at this temperature. The mean molecular weight of the pyrolysis gases would be expected to decrease further with increasing char temperature and more nearly approach equilibrium as the two high molecular weight products, benzene and cyclopentanone, crack to lower molecular weight products. The increasing differences, observed between the two curves
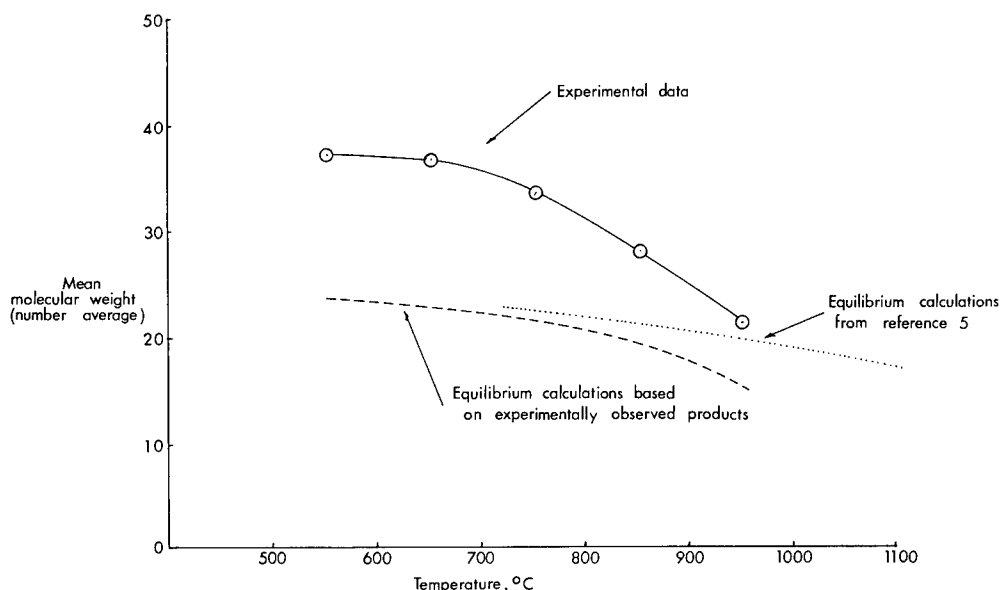
Figure 9.- Effect of char temperature upon the mean molecular weight
of the pyrolysis products.

obtained from equilibrium calculations, result from the loss of species found in the exper-
imental investigation. These losses (indicated in table IV) can occur from formation of
new unidentified gaseous products and from carbon deposition. The results of figure 9
would imply that in a real char layer where temperatures usually are considerably above
950° C, chemical equilibrium would be approached. However, because flow velocities
are much higher in a real char layer, this implication is not necessarily valid.

Carbon Deposition

There are two general types of carbon deposition which have been found to occur
when hydrocarbon gases flow through a porous material at high temperature. (See
ref. 12.) The first type occurs when the incoming gas (hydrocarbon) is relatively cool
and impinges upon a hot surface; the hydrocarbon gas is cracked at the surface and car-
bon is deposited on the surface. Pyrolytic carbon results from this type of deposition
and reference 2 presents an example of pyrolytic deposition on a porous carbon when
methane was cracked on the pore surfaces. The second type of deposition that can occur
results when incoming gas molecules are heated in the gas phase and are cracked before
striking the hot surface. This type of carbon formation can also lead to deposition on the
hot surface. However, the deposition that occurs under these conditions is loosely
attached and has an unordered nature as opposed to the regular ordered pyrolytic-type
deposition. Both of these types of deposition have been observed when studying the flow
of hydrocarbon gases through heated carbon. In the present investigation, many different
organic products from decomposition are flowing through the carbon char. It is possible

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that part of the unidentified products (16 percent) could be extremely high boiling point products and therefore condense at lower temperatures (char temperatures of 550° C to 650° C). These same products could thermally decompose when the char is heated to higher temperatures, leave a carbon residue, and thus lead to a third type of deposition.

After an analysis of the cracking pattern of the pyrolysis gases was made, the porous carbon char was analyzed by photomicrograph techniques to determine the extent and type of carbon deposition. Deposition was found as shown in figures 10, 11, and 12.
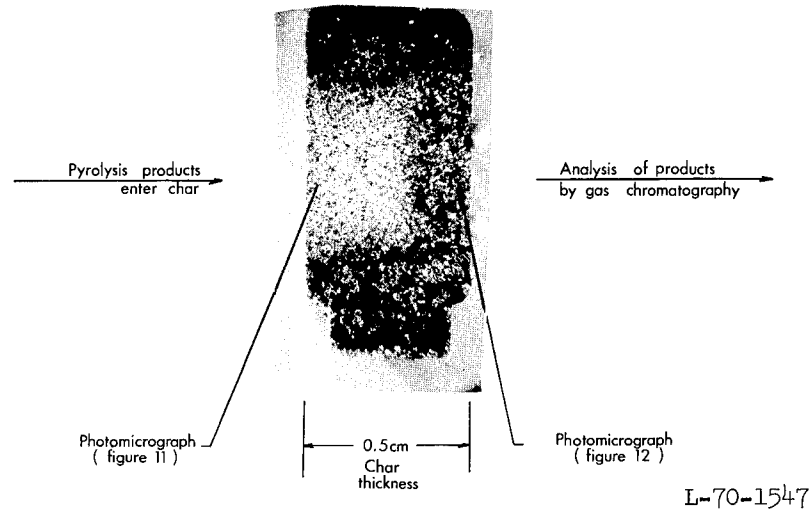

Pyrolysis products enter char

Analysis of products by gas chromatography

Photomicrograph (figure 11)

0.5 cm Char thickness

Photomicrograph (figure 12)

L-70-1547

Figure 10.- Photograph of carbon specimen showing flow region through center and location of photomicrograph.

Epoxy filled void
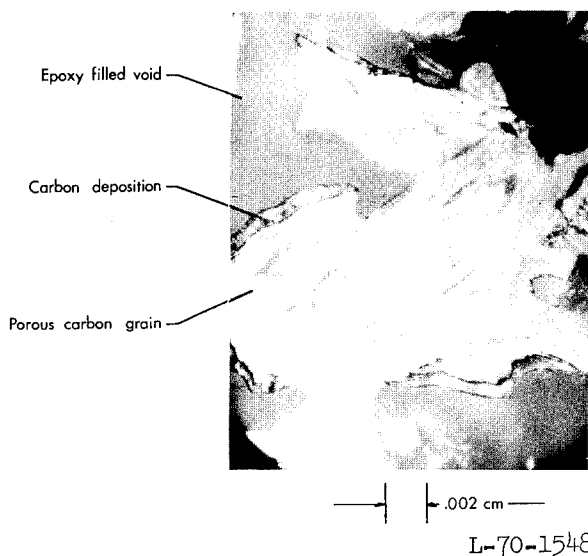
Carbon deposition

Porous carbon grain

.002 cm

L-70-1548

Figure 11.- Photomicrograph of porous carbon near entrance face.

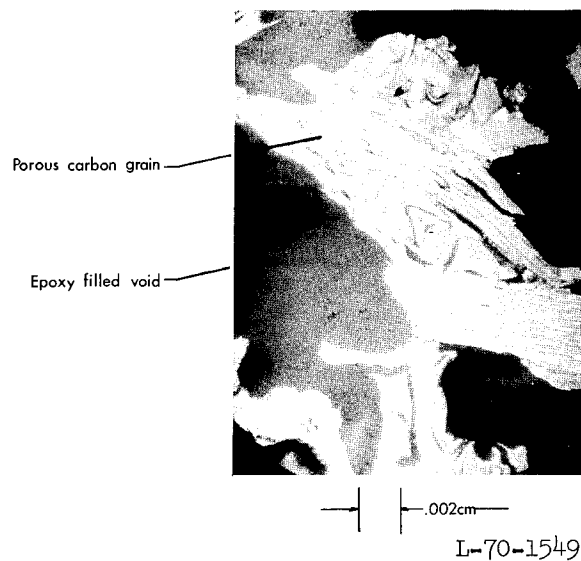Porous carbon grain

Epoxy filled void

.002 cm

L-70-1549

Figure 12.- Photomicrograph of porous carbon near exit face.

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Figure 10 shows the char specimen after vacuum molding in epoxy and polishing for photomicrograph studies. The flow pattern through the char can be seen by the reflective area through the center of the char. The light area (reflective area) is believed to result from carbon deposition; it is more intense from the left face to the center of the char (pyrolysis products enter the left face) and diminishes toward the right side of the char. The flow pattern also indicates that a good seal was obtained between the char and quartz tubing. Photomicrographs were taken at the front face and exit face of the char specimen and are shown in figures 11 and 12. Figure 11 shows the photomicrograph taken near the left face at a point just below the surface in the center of the char specimen. The photomicrograph shows a dark smoothed layer on the pore surface that was observed through the center of the char specimen. The deposited layer shows no ordered stacking of carbon, as observed in the pyrolytic deposition of reference 2. This condition indicates that the cracking reactions occurred in the gas phase or resulted from deposition and subsequent cracking of the condensed specie. No attempts were made to evaluate the thickness of deposition on the pore surfaces. Figure 12 shows the photomicrograph of an area near the exit face of the specimen. This area is typified by sharp well-defined surface pore edges and no deposition was found.

As described in a previous section, a differential pressure transducer was installed across the char specimen to determine the extent of pore closure as the products of pyrolysis passed through the char. Figure 13 shows the increase and decrease in upstream pressure that occurred as the products passed through the char. As shown, there was an immediate pressure increase in front of the char as the products were generated by flash pyrolysis of the heat-shield material. The large increase in pressure in front of the char was followed by successive pressure pulses from one side of the char to the other side until approximately 1.5 to 2.0 minutes after pyrolysis. After establishing a suitable baseline (approximately 3 minutes after pyrolysis) the change in Δp (difference between initial value and final value) was determined. The test results shown in figure 13 resulted in a 2.7-N/m^2 change, when the char was at 850° C. Changes of this magnitude were observed when the char temperature was 850° C and 950° C. Larger changes in differential pressure were not observed and consistent data could not be obtained.
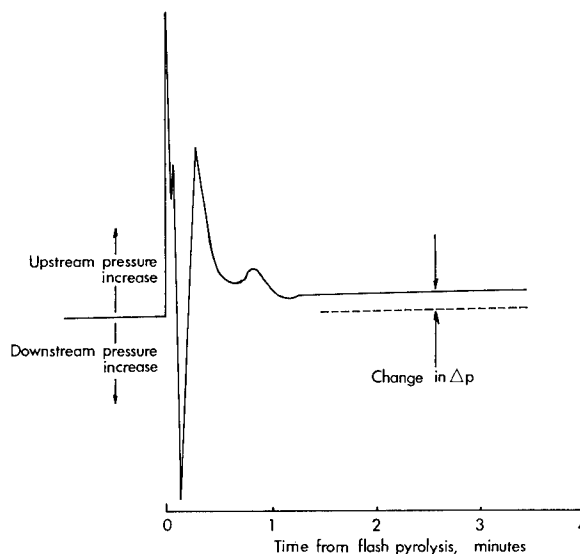

Figure 13.- Differential pressure fluctuations observed as the pyrolysis products pass through the porous carbon char at 850° C.

CONCLUSIONS

An analysis of the thermal cracking of phenolic-nylon pyrolysis products has been performed. The pyrolysis products were generated by flash pyrolysis and were analyzed by gas chromatography after passing through a simulated char at isothermal temperatures to about 1000° C. The results have led to the following conclusions:

1. The composition of the pyrolysis gases of phenolic-nylon change with char temperature beginning at about 650° C.

2. The number average molecular weight of the pyrolysis gases decreased from 37 to about 21 as the char temperature increased to 950° C.

3. At 950° C the products present, in order of decreasing quantities, are carbon dioxide, benzene, carbon monoxide, cyclopentanone, methane, hydrogen, water, and acetylene.

4. The cracking pattern of the high molecular weight products of phenolic decomposition resulted in a large quantity of benzene as the char temperature approached 950° C.

5. Carbon deposition was observed to result from cracking of pyrolysis products on passing through the carbon char.

6. The results of product analysis after passing through the char indicate that at a flow velocity of 0.83 cm^3/sec, the gas composition is approaching chemical equilibrium.

Langley Research Center,
    National Aeronautics and Space Administration,
        Hampton, Va., March 25, 1970.

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